

412 Rec'd PCT/PTO 08 MAR 2000

LAW OFFICES
SUGHRUE, MION, ZINN, MACPEAK & SEAS, PLLC 09/508252

2100 PENNSYLVANIA AVENUE, N.W.
WASHINGTON, D.C. 20037-3202
TELEPHONE (202) 293-7060
FACSIMILE (202) 293-7860

CALIFORNIA OFFICE

1010 EL CAMINO REAL
MENLO PARK, CA 94025
TELEPHONE (650) 325-5800
FACSIMILE (650) 325-6606

ATTN: BOX PCT

Assistant Commissioner for Patents
Washington, D.C. 20231

March 8, 2000

JAPAN OFFICE

TOEI NISHI SHIMBASHI BLDG. 4F
13-5 NISHI SHIMBASHI 1-CHOME
MINATO-KU, TOKYO 105, JAPAN
TELEPHONE (03) 3503-3760
FACSIMILE (03) 3503-3756



ATTN: BOX PCT

Re: Application of Michio ASANO, Kenji FUTATSUGI and Masayuki TSUJI
**LOW-ELECTROSTATICALLY-CHARGING GRANULAR POLYTETRAFLUOROETHYLENE
POWDER AND PREPARATION PROCESS OF SAME**
Our Reference: Q58192
PCT/JP98/03946, filed September 3, 1998

Dear Sir:

Applicants herewith submit the attached papers for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty. Attached hereto is the application identified above which is a translation of PCT International Application No. PCT/JP98/03946, filed September 3, 1998, comprising the specification, claims, one (1) sheet of drawing, executed Declaration and Power of Attorney, Preliminary Amendment, foreign language International Preliminary Examination Report, Information Disclosure Statement, PTO Form 1449 with references, International Search Report, executed Assignment and PTO Form 1595.

The Government filing fee, after consideration of the attached Preliminary Amendment, is calculated as follows:

Total Claims	10 - 20 =	0 x \$18 =	\$ 000.00
Independent Claims	2 - 3 =	0 x \$78 =	\$ 000.00
Base Filing Fee	(\$840.00)		\$ 840.00
Multiple Dep. Claim Fee	(\$260.00)		\$ 000.00
TOTAL FILING FEE			\$ 840.00
Recordation of Assignment Fee			\$ 40.00
TOTAL U.S. GOVERNMENT FEE			\$ 880.00

Checks for the statutory filing fee of \$ 840.00 and Assignment recordation fee of \$ 40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. 1.492; 1.16 and 1.17 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Japanese Patent Application
243138/1997

Filing Date
September 8, 1997

The Office is invited to contact the above firm on any question which might arise on the above-named application. Any contact that the Office might need to make should be directed to Abraham J. Rosner, Registration No. 33,276, at (202)293-7060.

Respectfully submitted,
SUGHRUE, MION, ZINN, MACPEAK & SEAS
Attorneys for Applicant(s)

By

Waddell A. Biggart
Registration No. 24,861

WAB:clf

09/508252
416 Rec'd PCT/PTO 08 MAR 2000
ATTN: BOX PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Michio ASANO, Kenji FUTATSUGI and Masayuki TSUJI

Serial No.: NOT YET ASSIGNED

PCT/JP98/03946, filed September 3, 1998

Filed: March 8, 2000

For: LOW-ELECTROSTATICALLY-CHARGING GRANULAR POLYTETRAFLUOROETHYLENE POWDER AND PREPARATION PROCESS OF SAME

PRELIMINARY AMENDMENT

ATTN: BOX PCT

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to examination of the above-identified application, please amend the above-mentioned application as follows:

IN THE CLAIMS:

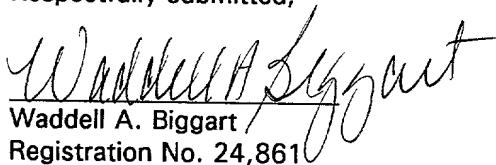
- Claim 3, line 1, delete "any of Claims 1 and 2," and insert therefor --Claim 1,--.
- Claim 4, line 1, delete "any of Claims 1 and 2," and insert therefor --Claim 1,--.
- Claim 5, line 1, delete "any of Claims 1 to 4," and insert therefor --Claim 1,--.
- Claim 7, line 1, delete "any of Claims 5 and 6," and insert therefor --Claim 5,--.
- Claim 10, line 1, delete "Claim 8 or 9," and insert therefor --Claim 8,--.

REMARKS

The above amendments are made to eliminate multiple dependent claims.

Applicants submit no questions of new matter should arise and entry is requested.

Respectfully submitted,


Waddell A. Biggart
Registration No. 24,861

SUGHRUE, MION, ZINN, MACPEAK & SEAS
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3202
Tel: (202) 293-7060
WAB:clf

Date: March 8, 2000

DESCRIPTION

LOW-ELECTROSTATICALLY-CHARGING GRANULAR
POLYTETRAFLUOROETHYLENE POWDER
AND PREPARATION PROCESS OF SAME

5

TECHNICAL FIELD

The present invention relates to a granular polytetrafluoroethylene (PTFE) powder having a low-electrostatically-10 charging property and a preparation process thereof.

BACKGROUND ART

PTFE, particularly PTFE prepared by suspension polymerization is, after once pulverized to an average particle size of not 15 more than 100 μm , granulated by various granulation methods such as a dry granulation method, a method of granulation in the state of emulsion, a granulation method in the state of aqueous dispersion and a method of granulation by wetting and if necessary, subjected to shaping into a granular powder having an average particle size of about 100 to 20 600 μm . The granular powder after the shaping is used as a molding powder for powder molding.

However since PTFE has electrically insulating property, it is easily charged when dry, its powder flowability is lowered and in addition, it sticks to a transportation pipe and a molding die. Once 25 PTFE powder sticks thereto, complicated steps are required when changing to other product, and it is impossible to change from PTFE to other product particularly when PTFE is transported through the pipe.

Therefore it is proposed that after granulation, a granular powder is treated with an aqueous solution of ion-dissociative substance (electrolyte) such as an inorganic acid or inorganic salt to electrically neutralize static electricity (JP-B-53-13230). However in that method, 5 though the charged granular PTFE powder can be once neutralized electrically, there is no effect on prevention of electrostatic re-charging caused by a friction at transporting and molding the powder after drying since the electrolyte is used.

The present inventors have found that a granular PTFE 10 powder granulated in the presence of a surfactant has unexpectedly low-electrostatically-charging property, and as a result of further investigations, have found that a polar group of the surfactant has a function to prevent electrostatic charging and exhibits an electrostatic charging-preventing ability at the time when the powder is substantially 15 dry, concretely when it is transported and is molded after drying. Thus the present invention was completed.

An object of the present invention is to provide a low- 20 electrostatically-charging granular PTFE powder which can maintain an electrostatic charging-preventing ability even after dried substantially, and a preparation process thereof.

DISCLOSURE OF THE INVENTION

The present invention relates to a process for preparing a low-electrostatically-charging granular PTFE powder by contacting a 25 granular PTFE powder to a polar group-containing organic compound having an electrostatic charging-preventing ability after the powder is dried substantially, and then drying the granular PTFE powder with the

polar group-containing organic compound being left contained in the powder.

In that preparation process, it is preferable that after the polar group-containing organic compound in the form of an aqueous 5 solution is contacted to the granular PTFE powder, the granular powder is dried without washing.

The effect of the present invention can be exhibited particularly when the granular PTFE powder contains no filler or when even if the filler is contained, the filler is an electrically insulating filler.

10 As a polar group-containing organic compound which has an electrostatically charging-preventing ability after dried substantially, preferred is a surfactant, particularly an anionic surfactant or nonionic surfactant. In case where the surfactant is used in the form of an aqueous solution, it is preferable that a content thereof is 1 to 30,000 15 mg/liter, particularly 25 to 10,000 mg/liter.

Further the present invention relates to the granular PTFE powder containing a polar group-containing organic compound in an amount of 10 to 300 ppm and having an electrostatic charge of not more than 50 V, preferably not more than 10 V.

20

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a diagrammatic view of an apparatus used for determining flowability of the granular powder in examples.

25

BEST MODE FOR CARRYING OUT THE INVENTION

The granulation method of the granular PTFE powder which can be used in the preparation process of the present invention is not

limited, and the granular PTFE powder can be prepared by various granulation methods (JP-B-44-22619, JP-B-44-22620, JP-B-60-21694, JP-A-3-259925, JP-A-9-52955, WO97/15611 and WO97/11111). Also the preparation process of the present invention is effectively applied 5 particularly to a granular PTFE powder containing no filler with the electrostatic charge problem and a granular PTFE powder containing an electrically insulating filler. With respect to a granular PTFE powder prepared by a granulation method using a surfactant at granulating, for example, a granulation method in the state of emulsion or PTFE 10 containing an electrically conductive filler, an amount of a polar group-containing organic compound having electrostatic charging-preventing ability (hereinafter in some cases referred to simply as "electrostatic charging-preventing compound") may be decreased.

JP-A-3-255133 discloses a method of removing a hydrophobic 15 filler sticking to a surface of a filler-containing granular PTFE powder by stirring and washing with an aqueous solution of a surfactant. However since this method intends to wash the filler on the granular PTFE powder with an aqueous solution of a surfactant, an electrostatic charging-preventing property seems not improved because the 20 surfactant is removed by washing with water after treatment. Further that patent publication discloses neither lowering of an electrostatic charging property nor electrical properties of the granular powder after treatment.

As PTFE used in the present invention, there may be used 25 tetrafluoroethylene homopolymer or a modified PTFE containing a copolymerizable component in an amount of not more than 5 % in a range not losing non-melt-processability. The granular powder may be

subjected to the treatment of the present invention for lowering electrostatic charge as it is after the granulation or after a step for shaping of the granular powder. The granular powder may be subjected to such treatment after once dried or in the form of being wetted with
5 water.

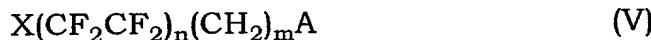
Filler-containing granular PTFE powders to be used are those prepared by known processes. As mentioned above, the present invention is applied effectively in case where a powder contains an electrically insulating filler which involves a problem with
10 electrostatically charging property. Examples of the electrically insulating filler are, for instance, inorganic fillers such as glass fiber and powder, molybdenum disulfide powder and fluorinated mica powder; organic fillers such as a wholly aromatic polyester resin powder, polyimide powder, polyphenylene sulfide powder and
15 tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymer powder; and the like. Examples of the electrically conductive filler are, for instance, metal fibers or metal powders such as bronze powder, gold powder, silver powder and stainless steel powder, coke powder, carbon fiber, and the like. Among them, it is preferable that hydrophilic fillers such as glass
20 fiber are previously surface-treated with a surface-treating agent such as aminosilane to be hydrophobic.

The electrostatic charging-preventing compound may be a polar group-containing organic compound having an electrostatic charging-preventing ability when substantially dry. Examples of the
25 preferred electrostatic charging-preventing compound are a surfactant, polymethyl methacrylate, polyurethane, and the like. Among them, a surfactant having no effect on physical properties of a fluorine-

containing resin is preferable.

As the surfactant, any of anionic, cationic and nonionic surfactants can be used. In the present invention, since a desired effect can be obtained by letting the surfactant remain in the granular powder, 5 anionic and nonionic surfactants, particularly a nonionic surfactant are preferable from the viewpoint of being easily kept remaining in a fluorine-containing resin.

As the anionic surfactant, there can be used known ones, for example, higher fatty acid and its salt, alkyl sulfate, alkyl sulfonate, 10 alkyl aryl sulfonate, alkyl phosphoric acid ester, and the like. Particularly preferable anionic surfactants are a sulfate of higher alkyl alcohol, for example, sodium lauryl sulfate or a fluorine-containing sulfonic acid type- or carboxylic acid type-anionic surfactant having a fluoroalkyl group or chlorofluoroalkyl group. The typical compounds 15 thereof are those represented by the formula (V):



or the formula (VI):

20



wherein X is hydrogen atom, fluorine atom or chlorine atom, n is an integer of 3 to 10, m is 0 or an integer of 1 to 4, A is carboxyl group, 25 sulfonic acid group or an alkali metal or ammonium residue thereof.

From the viewpoint that coloration of a molded article is difficult to arise when it is sintered by heating, an anionic surfactant

having a perfluoroalkyl group or perchlorofluoroalkyl group as a hydrophobic group is preferable.

Examples of the polar group of the anionic surfactant are a sulfonic acid group, sulfuric acid ester group, phosphoric acid ester group, and the like.

Examples of the above-mentioned nonionic surfactant are, for instance, polyoxyethylamine oxides, alkylamine oxides, polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, glycerine esters, polyoxyethylene alkylamine, segmented polyalkylene glycols having a hydrophobic segment comprising poly(oxyalkylene) unit having 3 or 4 carbon atoms and a hydrophilic segment comprising poly(oxyethylene) unit, the derivatives thereof, and the like.

More particularly, examples of the polyoxyethylamine oxides are dimethyloxyethylamine oxide, and the like.

Examples of the alkylamine oxides are dimethyllaurylamine oxide, dimethyloleylamine oxide, and the like.

Examples of the polyoxyethylene alkyl ethers are polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene behenyl ether, and the like.

Examples of the polyoxyethylene alkyl phenyl ethers are polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, and the like.

Examples of the polyoxyethylene fatty acid esters are polyoxyethylene monolauric acid ester, polyoxyethylene monooleic acid

ester, polyoxyethylene monostearic acid ester, and the like.

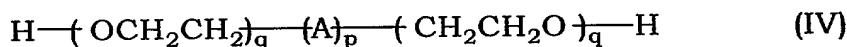
Examples of the sorbitan fatty acid esters are sorbitan monolauric acid ester, sorbitan monopalmitic acid ester, sorbitan monostearic acid ester, sorbitan monooleic acid ester, and the like.

5 Examples of the polyoxyethylene sorbitan fatty acid esters are polyoxyethylene sorbitan monolauric acid ester, polyoxyethylene sorbitan monopalmitic acid ester, polyoxyethylene sorbitan monostearic acid ester, and the like.

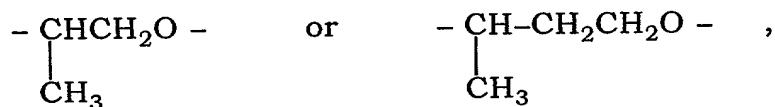
10 Examples of the glycerine esters are monomyristic acid glyceryl, monostearic acid glyceryl, monooleic acid glyceryl, and the like.

Examples of the derivatives of the above surfactants are, for instance, polyoxyethylene alkyl phenyl-formaldehyde condensate, polyoxyethylene alkyl ether phosphate, and the like.

15 As the segmented polyalkylene glycols having a hydrophobic segment and hydrophilic segment, preferable are, for example, those represented by the formula (IV):

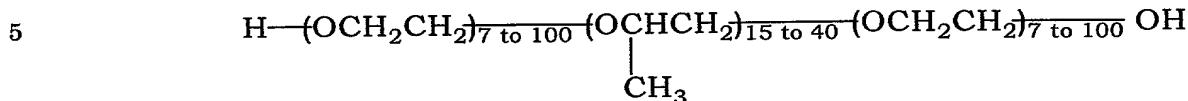


20 wherein A is



25 p is an integer of 5 to 200, q is an integer of 2 to 400. From the viewpoint of being easily adsorbed in the PTFE resin, it is preferable that p is from 15 to 40 and q is from 7 to 100.

Among them, preferable are amine oxides, polyoxyethylene alkyl phenyl ethers and segmented polyalkylene glycols. Further preferable are polyoxyethylamine oxide and



From the viewpoint that coloration of a molded article is difficult to arise when it is sintered by heating, a nonionic surfactant 10 having a hydrophobic segment comprising poly(oxyalkylene) unit having 3 or 4 carbon atoms and a hydrophilic segment comprising poly(oxyethylene) unit is preferable.

Examples of the polar group of the nonionic surfactant are a polyoxyethylene moiety, polyoxypropylene moiety, polyoxybutylene moiety, and the like.

Examples of the cationic surfactant are, for instance, polyvinylbenzyltrimethylammonium chloride, a quaternary compound of polydimethylaminoethyl methacrylate, polydiallyldimethylammonium chloride, and the like.

20 Example of the polar group of the cationic surfactant is an ammonium salt moiety.

As a method of contacting an electrostatic charging-preventing compound to a granular PTFE powder, there are:

(1) a method of pouring the granular PTFE powder into an aqueous
25 solution of electrostatic charging-preventing compound,
(2) a method of spraying an aqueous solution of electrostatic charging-
preventing compound to the granular PTFE powder,

(3) a method of pouring an electrostatic charging-preventing compound into a granulation tank immediately after granulation (shaping) of the granular PTFE powder,
and the like method. Among them, from the viewpoint of production
5 cost, the method (3) is preferable.

By making such a contact, the electrostatic charging-preventing compound is stuck to the granular PTFE powder. The granular PTFE powder is dried with the electrostatic charging-preventing compound being stuck to and remaining on the granular
10 PTFE powder, if necessary, after separating an excess aqueous solution of the electrostatic charging-preventing compound.

In the present invention, since the electrostatic charging-preventing compound is required to be kept remaining on the granular PTFE powder, it is not particularly necessary to wash the powder with
15 water, etc. after the contact.

It is preferable that an amount of the electrostatic charging-preventing compound remaining on the granular PTFE powder is from 10 to 300 ppm, particularly from 20 to 150 ppm on the basis of the granular PTFE powder. When the remaining amount is in the above-mentioned range, it is possible to decrease an electrostatic charge of the
20 granular PTFE powder to not more than 50 V, preferably not more than 30 V, particularly not more than 10 V.

According to the preparation process of the present invention, it is possible to prevent the granular PTFE powder from being
25 electrostatically charged even after dried substantially without lowering inherent properties of the granular PTFE powder, from lowering powder flowability and from sticking to a die for molding.

The preparation process of the present invention is then explained by means of examples, but the present invention is not limited to them.

5 The properties evaluated in examples and comparative examples are determined by the following methods.

Apparent density: Measured according to JIS K 6891-5.3.

Average particle size after pulverization (Primary particle size):

Wet sieve method: JIS standard sieves of 20 mesh (sieve opening: 840 μm), 250 mesh (sieve opening: 62 μm), 270 mesh (sieve opening: 53 μm), 325 mesh (sieve opening: 44 μm) and 400 mesh (sieve opening: 37 μm) are used. First, the 20 mesh sieve is placed on the 250 mesh sieve, and 5 g of a sample powder is put on the 20 mesh sieve. By spraying carbon tetrachloride carefully with a sprayer at a rate of about 3 liters/ m^2 for about 30 seconds, the powder is rinsed on the lower sieve. 15 When the sample powder has been rinsed completely, the upper sieve is removed and spraying all over the lower sieve is conducted for about four minutes. After that, the lower sieve is air-dried and a weight of the dried powder remaining thereon is measured. A series of the above-mentioned steps are repeated by using the 20 mesh sieve and each of the 20 other three sieves of smaller meshes, respectively, and 5 g each of new sample powder is used. In order to obtain an accumulated weight percentage, the weights of the powder remaining on each sieve are multiplied by 20 and then those obtained values are plotted on a logarithmic probability paper to openings of each sieve. Those plotted 25 points are connected with a line, particle sizes corresponding to the accumulated weight percentages 50(d_{50}) and 84(d_{34}) are read, and wet sieve size (d_{ws}) is calculated by the following equation.

$$\log_e d_{ws} = \log_e d_{50} - \frac{1}{2} \left(\log_e \frac{d_{34}}{d_{50}} \right)^2$$

Flowability: Measured in accordance with the method described in JP-A-3-259925.

5 Namely, there is used a measuring apparatus comprising a support base 42, an upper hopper 31 and a lower hopper 32. The both hoppers are aligned on their center lines and supported on the support base 42 as shown in Fig. 1 (corresponding to Fig. 3 described in JP-A-3-259925). The upper hopper 31 has an inlet 33 of 74 mm diameter, an
10 outlet 34 of 12 mm diameter and a partition plate 35. The height from the inlet 33 to the outlet 34 is 123 mm. The partition plate 35 is provided on the outlet 34, and thereby the powder in the hopper can be kept therein and dropped optionally. The lower hopper 32 has an inlet 36 of 76 mm diameter, an outlet 37 of 12 mm diameter and a partition
15 plate 38. The height from the inlet 36 to the outlet 37 is 120 mm, and the partition plate 38 is provided on the outlet 37 like the upper hopper. The upper hopper and the lower hopper are adjusted so that the distance between the both partition plates is 15 cm. In Fig. 1, numerals 39 and 40 represent outlet covers of each hopper, and numeral 41 represents a
20 vessel for receiving the dropped powder.

25 Prior to measuring the flowability, about 200 g of powder is allowed to stand for not less than four hours in a room, the temperature of which is adjusted to 23.5° to 24.5°C, and then sieved with a 10 mesh sieve (sieve opening: 1,680 µm). The measurement of the flowability is carried out at the same temperature.

(I) At first, immediately after the upper hopper 31 is charged with just a cup of powder by using a 30 cc cup, the partition plate 35 is pulled out to

drop the powder into the lower hopper. When the powder does not drop, the powder is stuck with a wire. After the powder has dropped completely into the lower hopper 32, the dropped powder is allowed to stand for 15 ± 2 seconds, and then the partition plate 38 of the lower hopper is pulled out to see whether or not the powder is dropped from the outlet 37. When the powder is dropped completely within eight seconds, the powder is estimated to have been dropped as required.

(II) The same steps as above are repeated three times to see if the powder is dropped as required. In case where the powder is dropped satisfactorily twice or more, the flowability of the powder is estimated to be "Good". In case where the powder is never dropped, the flowability of the powder is estimated to be "Not good". In case where in three series of the dropping test, the powder has been dropped only one time, the dropping test is further conducted twice, and when the two series of the dropping test are both satisfactory, the flowability is estimated to be "Good". In other cases, the flowability is estimated to be "Not good".

(III) With respect to the powder estimated to be "Good", the upper hopper is charged with two cups of powder by using the same 30 cc cup, and the dropping test of the powder is conducted in the same manner as above. When as a result, the flowability is estimated to be "Good", the number of cups filled with the powder is increased successively and the dropping test is continued until the flowability is estimated to be "Not good". The dropping test is conducted up to eight cups at most. The powder having flowed out from the lower hopper in the previous dropping test may be re-used.

(IV) The larger the amount of the PTFE powder is, the more difficult to drop.

The number of cups when the flowability is estimated to be "Not good" is subtracted by 1, and the obtained value is taken as "Flowability" of the powder.

Average particle size and particle size distribution of granular powder:

5 Standard sieves of 10, 20, 32, 48, 60 and 80 meshes (inch mesh) are placed in that order from the top, and granular PTFE powder is put on the 10 mesh sieve. The sieves are vibrated to drop smaller particles downward through each sieve in order. Then after the ratio of the powder remaining on each sieve is obtained by %, accumulated
10 percentages (ordinate) of each remaining powder to the openings of each sieve (abscissa) are plotted on the logarithmic probability paper, and those points are connected with a line. The particle size, the proportion of which is 50 % on that line, is obtained and is regarded as an average particle size. Also percents by weight of the granular powder remaining
15 on each sieve of 10, 20, 32, 48, 60 and 80 meshes are regarded as the particle size distribution.

Remaining amount of electrostatic charging-preventing compound: 50 Grams of a granular PTFE powder is put in Vial bottle, and after the bottle is sealed, the powder is heated at 200°C for 60 minutes to give a
20 sample. Then 5 cc of a sample gas is collected from the Vial bottle by means of an injector, and an amount of the electrostatic charging-preventing compound is determined by gas chromatography.

Electrostatic charge: Handy Electrostatic Meter SFM775 available from Ion Systems, Inc. is used to determine an electrostatic charge.

25 Tensile strength (hereinafter may be referred to as "TS") and elongation (hereinafter may be referred to as "EL"): A die having an inner diameter of 100 mm is charged with 25 g of powder, and a pressure is applied

gradually over about 30 seconds until the final pressure becomes about 300 kg/cm². Then that pressure is kept for two minutes to give a pre-molded article. The pre-molded article is taken out of the die mold and put in an electric oven being kept at 365°C to be subjected to sintering

5 for three hours. Then the sintered article is punched with a JIS dumbbell No. 3 to give a sample. A stress at break and elongation of the sample are measured in accordance with JIS K 6891-5.8 by stretching at a stretching rate of 200 mm/min with an autograph having a gross weight of 500 kg.

10 Whiteness (Z value): A 50 mm diameter die is filled with 200 g of a granular powder which is then maintained at a molding pressure of 300 kg/cm² for five minutes. The obtained pre-molded article (diameter: about 50 mm, thickness: 50 mm) is heated up from room temperature to 365°C at a temperature raising rate of 50°C/hr. After having been

15 maintained at 365°C for 5.5 hours, the pre-molded article is cooled at a cooling rate of 50°C/hr and then the molded article is cut crosswise with a lathe at the point about 25 mm from its end (center portion). Then the Z value on the center of the cut portion is measured through Z value measuring method of the XYZ colorimetric system of Commission

20 International de Leclairage.

EXAMPLES 1 to 4

A 200-liter granulation tank equipped with cone blades was charged with 120 to 150 liters of ion-exchanged water, and the inside

25 temperature of the tank was adjusted to 20° to 28°C. Then the tank was charged with 30 kg of PTFE powder (POLYFLON TFE MOLDING POWDER M-12 available from DAIKIN INDUSTRIES, LTD., TFE homopolymer)

prepared by suspension polymerization and pulverized into an average particle size of 34 μm . The corn blades were rotated at 400 rpm, and two to three minutes after, 19.1 kg of CH_2Cl_2 as an organic liquid was added in the tank. Subsequently the stirring was carried out at 400 rpm for five minutes to make the organic liquid and PTFE powder compatible with each other. After that, a product in the granulation tank was passed through a line mixer outside the tank for external circulation for ten minutes. The inside temperature of the tank was raised to 37° to 38°C over 15 minutes and kept at that temperature for 60 minutes to distil off the organic liquid and give a granular PTFE powder. Physical properties of the obtained granular PTFE powder and physical properties of a molded article obtained from the granular PTFE powder were determined by the above-mentioned methods. The results are shown in Table 1.

The granular PTFE powder was subjected to the following treatment for lowering its electrostatically charging property.

A 5 % aqueous solution of surfactant was added to an aqueous dispersion of the above-mentioned granular PTFE powder in a concentration shown in Table 1 (concentration on the basis of the granular PTFE powder), followed by stirring for five minutes.

After the stirring was stopped, the granular powder was separated from water by using a 150 mesh sieve, and a collected granular powder was dried at 165°C for 20 hours by using a box type hot air circulating dryer without washing with water to give the granular PTFE powder of the present invention which was subjected to treatment for lowering its electrostatically charging property.

Physical properties of the obtained granular PTFE powder

which was subjected to the treatment for lowering its electrostatically charging property and physical properties of a molded article obtained from the granular PTFE powder were determined by the above-mentioned methods. The results are shown in Table 1.

5 Surfactants shown in Table 1 are those mentioned below.

DS-101: Ammonium perfluorooctanoate which is an anionic surfactant available from DAIKIN INDUSTRIES, LTD.

Puronon #208: A nonionic surfactant available from NOF Corporation and represented by the following formula:

10

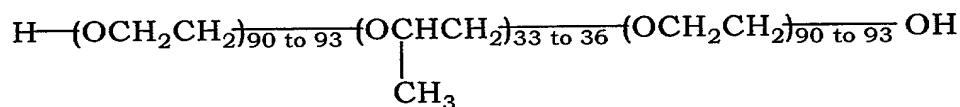


TABLE 1

	Ex. 1		Ex. 2		Ex. 3		Ex. 4	
	Before treated	After treated	Before treated	After treated	Before treated	After treated	Before treated	After treated
Conditions for treating for lowering electrostatically charging property								
Kind of surfactant	-	DS-101	-	DS-101	-	Puronon #208	-	Puronon #208
Concentration of surfactant (% by weight based on granular PTFE powder)	-	0.05	-	0.1	-	0.025	-	0.05
Physical properties of granular powder								
Apparent density (g/cm ³)	0.83 8.0	0.83 7.0	0.82 8.0	0.82 7.0	0.85 8.0	0.85 8.0	0.83 8.0	0.83 8.0
Flowability	320.0	20.0	330.0	300.0	3.0	3.0	310.0	0.0
Electrostatic charge (V)								
Particle size distribution (% by weight)								
10 on	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20 on	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
32 on	4.0	4.4	5.0	5.4	6.6	6.7	4.1	4.0
48 on	54.4	54.7	48.2	48.0	53.3	53.4	50.1	50.2
60 on	21.8	20.5	17.8	17.6	16.5	16.2	18.0	18.1
80 on	16.2	15.6	23.5	23.1	17.5	17.4	20.1	19.9
80 pass	3.6	4.8	5.5	5.9	6.1	6.3	7.7	7.8
Average particle size (μm)	340	330	310	340	340	340	310	310

- continued -

- continued -

Amount of remaining electrostatic charge-preventing compound (ppm)	57	-	110	-	62	-	70
Physical properties of molded article							
TS (kg/cm ² G)	430	390	400	400	390	390	400
EL (%)	400	380	390	390	390	390	390
Whiteness (Z value)	110.1	110.1	110.0	110.0	111.0	111.0	111.1

In the column of the particle size distribution of Table, 10 on, 20 on, 32 on, 48 on, 60 on and 80 on indicate the percentages of particles remaining on the 10 mesh, 20 mesh, 32 mesh, 48 mesh, 60 mesh and 80 mesh sieves, respectively. And, 80 pass represents the 5 percentage of the particles passed through the 80 mesh sieve.

EXAMPLE 5

9.90 Kg (dry basis) of a PTFE powder (POLYFLON TFE MOLDING POWDER M-111 available from DAIKIN INDUSTRIES, LTD.:

10 modified PTFE) having an average particle size of 25 μm after pulverizing and 1.10 kg of a glass fiber (average diameter: 12 μm , average fiber length: 80 μm) subjected to water repellent treatment previously with an aminosilane coupling agent were pre-mixed by using a 75-liter Henschel mixer.

15 A 10-liter granulation tank was charged with 6 liters of ion-exchanged water and 2 kg of the above-mentioned mixture obtained by pre-mixing the PTFE powder and glass fiber. Thereto was added 1,200 ml of methylene chloride (organic liquid forming a liquid-liquid interface with water), followed by stirring at 800 rpm at $25^\circ\text{C} \pm 2^\circ\text{C}$ for five minutes 20 with cone blades for granulation.

Further the stirring was continued at 2,000 rpm for two minutes by using dispersing blades of 100 mm diameter.

Then after shaping of the powder was carried out at $25^\circ\text{C} \pm 2^\circ\text{C}$ for ten minutes under stirring at 800 rpm with cone blades, the 25 inside temperature of the tank was raised up to 38°C over 20 minutes to give a granular PTFE powder. Physical properties of the obtained granular PTFE powder and physical properties of a molded article

obtained from the granular PTFE powder were determined by the above-mentioned methods. The results are shown in Table 2.

The obtained granular PTFE powder was subjected to the following treatment for lowering its electrostatically charging property.

5 To the aqueous dispersion of the above-mentioned granular PTFE powder was added a 5 % aqueous solution of Puronon #208 which is a nonionic surfactant, in a concentration shown in Table 1, followed by stirring at 400 rpm for five minutes. After the stirring was stopped, the granular powder was separated by using a 150 mesh sieve and the
10 collected granular powder was dried at 165°C for 16 hours with a box type hot air circulation dryer without washing with water, thus giving a filler-containing granular PTFE powder subjected to treatment for lowering electrostatically charging property.

Physical properties of the obtained granular PTFE powder
15 subjected to treatment for lowering electrostatically charging property and physical properties of a molded article obtained from the granular PTFE powder were determined by the above-mentioned methods. The results are shown in Table 2.

20

EXAMPLE 6

9.90 Kg (dry basis) of a modified PTFE powder (POLYFLON TFE MOLDING POWDER M-111 available from DAIKIN INDUSTRIES, LTD.) having an average particle size of 25 μm after pulverizing and 1.10 kg of a wholly aromatic polyester resin powder (ECONOL available from
25 Sumitomo Chemical Industries, Ltd., finely pulverized powder, average particle size: 30 to 40 μm) were pre-mixed by using a 75-liter Henschel mixer.

A 10-liter granulation tank was charged with 6 liters of ion-exchanged water and 2 kg of the mixture obtained by the above-mentioned pre-mixing of the PTFE powder and ECONOL. Thereto was added 1,200 ml of methylene chloride (organic liquid forming a liquid-5 liquid interface with water), followed by stirring at 800 rpm at 25°C ± 2°C for five minutes with cone blades for granulation.

Further the stirring was continued at 2,000 rpm for two minutes by using dispersing blades of 100 mm diameter.

Then after shaping of the powder was carried out at 25°C ± 10 2°C for ten minutes under stirring at 800 rpm with cone blades, the inside temperature of the tank was raised up to 38°C over 20 minutes to give a granular PTFE powder. Physical properties of the obtained granular PTFE powder and physical properties of a molded article obtained from the granular PTFE powder were determined by the 15 above-mentioned methods. The results are shown in Table 2.

The obtained granular PTFE powder was subjected to the following treatment for lowering electrostatically charging property.

To the aqueous dispersion of the above-mentioned granular PTFE powder was added a 5 % aqueous solution of sodium 20 tetradecenesulfonate (SOS) which is an anionic surfactant, in a concentration shown in Table 2, followed by stirring at 400 rpm for five minutes. After the stirring was stopped, the granular powder was separated by using a 150 mesh sieve and the collected granular powder was dried at 165°C for 16 hours with a box type hot air circulation dryer 25 without washing with water, thus giving a filler-containing granular PTFE powder subjected to treatment for lowering electrostatically charging property.

Physical properties of the obtained granular PTFE powder subjected to the treatment for lowering electrostatically charging property and physical properties of a molded article obtained from the granular PTFE powder were determined by the above-mentioned methods. The results are shown in Table 2.

TABLE 2

	Ex. 5		Ex. 6	
	Before treated	After treated	Before treated	After treated
Conditions for treating for lowering electrostatically charge property				
Kind of surfactant	-	Puronon #208	-	SOS
Concentration of surfactant (% by weight based on granular PTFE powder)	-	0.025	-	0.025
Characteristics of granular powder				
Apparent density (g/cm ³)	0.76	0.76	0.70	0.70
Flowability	8.0	8.0	8.0	8.0
Electrostatic charge (V)	120.0	0.0	220.0	0.0
Particle size distribution (%)				
10 on	0.0	0.0	0.0	0.0
20 on	5.8	6.0	16.3	16.4
32 on	47.9	49.7	32.5	32.9
48 on	39.7	39.6	30.0	29.7
60 on	5.1	3.4	9.7	9.6
80 on	1.1	1.0	8.0	7.8
80 pass	0.4	0.4	2.5	2.6
Average particle size (μm)	540	540	500	500
Remaining amount of electrostatic charge-preventing compound (ppm)	-	60	-	68
Physical properties of molded article				
TS (kgf/cm ² G)	160	160	160	1190
EL (%)	328	328	300	3
Whiteness (Z value)	96.7	96.7	-	111.1

INDUSTRIAL APPLICABILITY

According to the present invention, electrostatic charging of the granular powder can be inhibited even after drying, and good powder flowability can be maintained at the time of transportation and molding.

CLAIMS

1. A process for preparing a low-electrostatically-charging granular polytetrafluoroethylene powder prepared by contacting a polar group-containing organic compound having an electrostatic charging-preventing ability when substantially dry to a granular polytetrafluoroethylene powder and then drying the granular powder while the polar group-containing organic compound is kept remaining in the powder.

10

2. The preparation process of Claim 1, wherein the polar group-containing organic compound having an electrostatic charging-preventing ability when substantially dry is contacted in the form of an aqueous solution to the granular polytetrafluoroethylene powder and 15 then the granular powder is dried without washing.

3. The preparation process of any of Claims 1 and 2, wherein the granular polytetrafluoroethylene powder does not contain a filler.

20

4. The preparation process of any of Claims 1 and 2, wherein the granular polytetrafluoroethylene powder contains an electrically insulating filler.

25

5. The preparation process of any of Claims 1 to 4, wherein the polar group-containing organic compound is a surfactant.

6. The preparation process of Claim 5, wherein the

DRAFTING: DRAFTING

surfactant is an anionic or nonionic surfactant.

7. The preparation process of any of Claims 5 and 6, wherein the surfactant is used in the form of an aqueous solution.

5

8. A granular polytetrafluoroethylene powder containing a polar group-containing organic compound in an amount of 10 to 300 ppm and having an electrostatic charge of not more than 50 V.

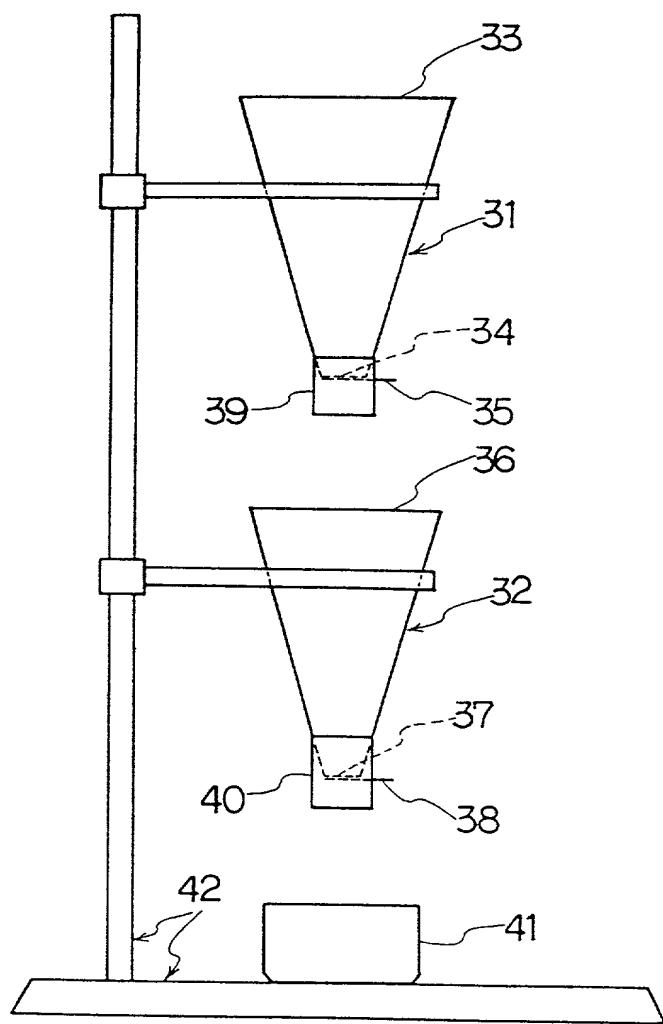
10 9. The powder of Claim 8, wherein the electrostatic charge is
not more than 10 V.

10. The powder of Claim 8 or 9, wherein the polar group-containing organic compound is a nonionic surfactant.

ABSTRACT

To provide a granular PTFE powder having a low electrostatic charging property even after drying. A process for preparing a low-
5 electrostatically-charging granular polytetrafluoroethylene powder by contacting a polar group-containing organic compound having an electrostatic charging-preventing ability when substantially dry to a granular polytetrafluoroethylene powder and then drying the granular powder while the polar group-containing organic compound is kept
10 remaining in the granular powder.

FIG. 1



DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

特許出願宣言書

Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下のとおり宣言する：

私の住所、郵便の宛先および国籍は、下欄に氏名に続いて記載したとおりであり、

名称の発明に關し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である(一人の氏名のみが下欄に記載されている場合)か、もしくは本来の、最初にして共同の発明者である(複数の氏名が下欄に記載されている場合)と信じ、

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

LOW-ELECTROSTATICALLY-CHARGING
GRANULAR POLYTETRAFLUOROETHYLENE
POWDER AND PREPARATION PROCESS
OF SAME

その明細所を
(該当する方に印を付す)

ここに添付する。

_____ 日に出願番号第
第 _____ 号として提出し、
_____ 日に補正した。
(該当する場合)

私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを探述する。

私は、連邦規則法典第37部第1章第56条(a)項に従い、本願の審査に所要の情報を開示すべき義務を有することを認める。

the specification of which
(check one)

is attached hereto

was filed on _____
as Appln. Ser. No. _____
and was amended on _____
(if applicable)

I hereby state that I have reviewed and understood the contents of the above-identified specification, including the claims, as amended by any amendments referred to above.

I acknowledge the duty to disclose information in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

と実よたら100にの憲しのとつ
も真おっさつ100錆ら故い許に行
にて報行、行第禁れるな持るを
識べ情てじを部はこか顧るあ述
知するつ信等18くはか本れが陳
のがす從と述第したたがさとの。
己述有にる陳典もまま述与こ上る
自陳のろあの法金、陳付う以す
にた己こで偽固罰かれのてな、言
こつ自と実虚衆、るさ偽し擅て宣
こ行、る真に合りれ科虚対をしを
、てりずが憲、よら併るに性識と
はいあ信述故合にせがよ顧効認こ
づでび陳に場条処刑に本有をた

し任と為と
と選こ行こ
者によるのう
明こす切行
発こ行 一て
記を述るし
下人をす対
、理統開に
は代手に序。
私ののれ標る
状以本に許任
任、、び特委
委てし並をを

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

I hereby appoint John H. Mion, Reg. No. 18,879; Donald E. Zinn, Reg. No. 19,046; Thomas J. Macpeak, Reg. No. 19,292; Robert J. Seas, Jr., Reg. No. 21,092; Darryl Mexic, Reg. No. 23,063; Robert V. Sloan, Reg. No. 22,775; Peter D. Olexy, Reg. No. 24,513; J. Frank Osha, Reg. No. 24,625; Waddell A. Biggart, Reg. No. 24,861; Robert G. McMorrow, Reg. No. 19,093; Louis Gubinsky, Reg. No. 24,835; Neil B. Siegel, Reg. No. 25,200; David J. Cushing, Reg. No. 28,703; John R. Inge, Reg. No. 26,916; Joseph J. Ruch, Jr., Reg. No. 26,577; Sheldon I. Landsman, Reg. No. 25,430; Richard C. Turner, Reg. No. 29,710; Howard L. Bernstein, Reg. No. 25,665; Alan J. Kasper, Reg. No. 25,426; Kenneth J. Burchfiel, Reg. No. 31,333; Gordon Kit, Reg. No. 30,764; Susan J. Mack, Reg. No. 30,951; Frank L. Bernstein, Reg. No. 31,484; Mark Boland, Reg. No. 32,197; William H. Mandir, Reg. No. 32,156; Scott M. Daniels, Reg. No. 32,562; Brian W. Hannon, Reg. No. 32,778; Abraham J. Rosner, Reg. No. 33,276; Bruce E. Kramer, Reg. No. 33,725; Paul F. Neils, Reg. No. 33,102; and Brett S. Sylvester, Reg. No. 32,765, my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that all correspondence about the application be addressed to **SUGHRUE, MION, ZINN, MACPEAK & SEAS**, 2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037-3202.

Full name of sole or first inventor Michio ASANO
唯一のまたは第一の発明者の氏名(ローマ字) Michio ASANO
Inventor's signature Michio Asano Date February 28, 2000
同発明者の署名 Michio Asano 日付 February 28, 2000
Residence Settsu-shi, OSAKA 566-8585 JAPAN Citizenship Japanese
住所 Settsu-shi, OSAKA 566-8585 JAPAN 国籍 Japanese
Post office address c/o Yodogawa-seisakusho, DAIKIN INDUSTRIES, LTD., 1-1,
郵便の宛先 Nishihiotsuya, Settsu-shi, OSAKA 566-8585 JAPAN

200
Full name of second joint inventor (if any) Kenji FUTATSUGI
第2の共同発明者の氏名(該当する場合)(ローマシ)
Second Inventor's signature Kenji FUTATSUGI Date February 28, 2000
同第2発明者の署名 Kenji FUTATSUGI 日付 February 28, 2000
Residence Settsu-shi, OSAKA 566-8585 JAPAN Citizenship Japanese
住所 Settsu-shi, OSAKA 566-8585 JAPAN 国籍 Japanese
Post office address c/o Yodogawa-seisakusho, DAIKIN INDUSTRIES, LTD., 1-1,
郵便の宛先 Nishihitotsuya, Settsu-shi, OSAKA 566-8585 JAPAN

300
Full name of third joint inventor (if any) Masayuki TSUJI
第3の共同発明者の氏名(該当する場合)(ローマシ)
Third Inventor's signature Masayuki Tsuji Date February 28, 2000
同第3発明者の署名 Masayuki Tsuji 日付 February 28, 2000
Residence Settsu-shi, OSAKA 566-8585 JAPAN Citizenship Japanese
住所 Settsu-shi, OSAKA 566-8585 JAPAN 国籍 Japanese
Post office address c/o Yodogawa-seisakusho, DAIKIN INDUSTRIES, LTD., 1-1,
郵便の宛先 Nishihitotsuya, Settsu-shi, OSAKA 566-8585 JAPAN

Full name of fourth joint inventor (if any)
第4の共同発明者の氏名(該当する場合)(ローマシ)
Fourth Inventor's signature _____ Date _____
同第4発明者の署名 _____ 日付 _____
Residence _____ Citizenship _____
住所 _____ 国籍 _____
Post office address _____
郵便の宛先 _____

Full name of fifth joint inventor (if any)
第5の共同発明者の氏名(該当する場合)(ローマシ)
Fifth Inventor's signature _____ Date _____
同第5発明者の署名 _____ 日付 _____
Residence _____ Citizenship _____
住所 _____ 国籍 _____
Post office address _____
郵便の宛先 _____

Full name of sixth joint inventor (if any)
第6の共同発明者の氏名(該当する場合)(ローマシ)
Sixth Inventor's signature _____ Date _____
同第6発明者の署名 _____ 日付 _____
Residence _____ Citizenship _____
住所 _____ 国籍 _____
Post office address _____
郵便の宛先 _____